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Preliminary Study of Bio-Metal Organic Frameworks (Bio-MOFs) Based Chromium-Citric Acid for CO₂ Adsorption Application

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Abstract: According to the Intergovernmental Panel on Climate Change (IPCC), carbon dioxide (CO₂) gas is one of the significant factors that caused climate change. In the IPCC's special report regarding Carbon Dioxide Capture and Storage, there was discussion about several technologies for CO₂ gas capture. One of the technologies is using solid sorbent such as activated carbon, silica, metal oxides, and zeolite. Recently, there has been a significant increase in the research of Metal Organic Frameworks (MOFs) which are believed to be the most promising adsorbent in CO₂ adsorption application. It is a crystalline type of porous material consisting of the metal ions and the organic ligands. With all the advantages possessed by MOFs, these adsorbents are still difficult to be applied on industrial scale due to high fabrication cost. Composed of non-renewable feedstock raw materials, some MOFs are not environmentally friendly. To quickly response this challenge, we conducted investigation on the use of biologically derived MOF (Bio-MOF) in CO₂ capture application. A novel of Bio-MOF Chromium-Citric Acid (Cr-CA) has been explored. The synthesis process is carried out through the hydrothermal reaction method using eco-friendly solvent potassium hydroxide and Aquabidest. The characterization of MOF was carried out by Brunauer-Emmett-Teller (BET), X-ray diffraction (XRD) testing, scanning electron microscope (SEM), thermal gravimetric analysis (TGA), and Fourier transform infrared spectroscopy (FTIR) analysis. We would like to recommend that research about MOF with Chromium-Citric Acid content is conducted and investigated further on the performance of gas adsorption with this porous material.

Keywords: Bio-MOFs; Citric Acid; Adsorbent characteristic; CO₂ Adsorption

1. Introduction

Carbon dioxide (CO₂) capture and storage (CCS) is a process consisting of the separation of CO₂ from the sources, transportation to the storage location and long-term isolation from the atmosphere maker^{1, 2}. Adsorption process is one of the CCS technologies that could be used to mitigate the climate change for reducing CO₂ in the atmosphere^{3, 4}. Pilot test results of coal-fired flue gas CO₂ recovery by adsorption processes show that CO₂ recovery is reaching about 99.0 by volume using two stages of pressure swing adsorption and temperature swing adsorption system. Compared to traditional adsorbents like zeolite, activated carbon, and silica which has drawbacks in high regeneration energy and low material resistance, Metal Organic Frameworks (MOFs) could be a substitute adsorbent in CCS system^{5, 6}.

MOF is a crystallized porous material consists of the combination of the metals and the ligands. MOF was first popularized in the 1990s and it has attracted the attention of scientists in the last two decades⁷. Aside from common

porous materials such as zeolites, silica, or activated carbon, MOF has special physical properties such as high thermal stability and porosity, easily controlled structure, and fast kinetic which make this type of adsorbent to be the most promising material that has been developed in various engineering branch applications such as natural gas, syngas, biogas in CO₂ removal⁸⁻¹⁰.

Most of the research and the usage of MOFs as sorbent in CO₂ adsorption uses raw materials derived from non-renewable petrochemical feedstocks which are not environmentally friendly¹¹. The need for environmentally friendly adsorbents, new research of bio-ligands as constituents of MOFs has begun to be explored. Biologically metal-organic frameworks (Bio-MOFs) with bio-ligand constituents have advantages such as being environmentally friendly, easy to produce, abundant availability, and having multiple reactive sites¹².

The challenge to develop MOF with the principle of renewability and recyclability with fabrication costs can be fulfilled by using Bio-MOF¹³. Therefore, in this study,

we tried to take advantage of the flexibility of ligands, citric acid, to build porous material with metal chromium nitrate. Bio-molecule citric acid derived from citrus fruits with high availability of raw materials has tricarboxylic acid structure which are expected to absorb more CO₂ molecules. By using this bio-ligand, the MOF fabrication cost will be much lower than other reported MOFs. The synthesized material will be characterized by various methods including XRD, SEM, BET, FTIR, and TGA to obtain the physical properties such as the crystallinity, the morphology, the porosity, the chemical functionalities, and the thermal stability. The results of this study are expected to be further investigated in CO₂ gas adsorption application^{14, 15}.

2. Methodology

This research is conducted by using chromium (III) nitrate nonahydrate [Cr(NO₃)₃·9H₂O] as the metal and citric acid monohydrate (C₆H₈O₇) as the ligand. The solvents are only using Aquabidest and Potassium Hydroxide (KOH) which is known to be more environmentally friendly than NaOH in adjusting the pH of the MOF solution¹⁶.

The synthesis process was carried out by referring to Xiang et al who produced MOF UTSA-16 with citric acid ligand with several modifications¹⁷. This synthesis process was conducted with hydrothermal reaction process with the composition of material mixture as following: Chromium Nitrate (2.5 gr), Citric Acid (2.1 gr), Potassium Hydroxide (1.7 gr), Ethanol (2.5 mL), and deionized water/Aquabidest (2.5 mL). Those materials were mixed and poured in the reactor inside the stainless-steel autoclave. The autoclave was heated gradually in the oven from the ambient temperature until reaching 120 °C in 30 minutes. After reaching 120°C, the temperature was maintained constant for 48 hours¹⁷.

When that process was completed, the reactor autoclave was cooled down gradually. After cooling down process, the crystal MOF would be obtained after centrifugation process was conducted. Dimethylformamide/DMF was added in the MOF to separate the excess ligand or any other substances which were not reacted with the MOF¹⁸.

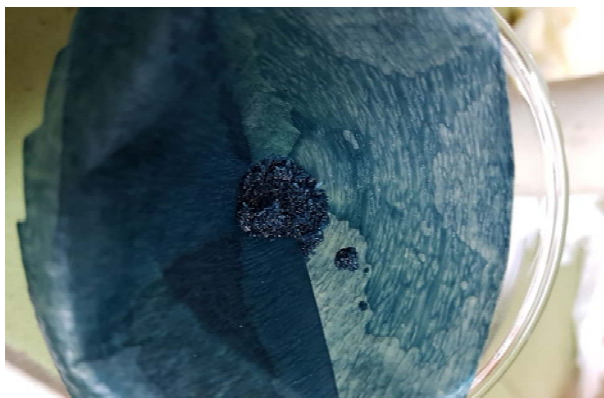


Fig. 1: final MOFs result after drying process

The MOF result was strained with the straining paper as could be seen in Fig. 1.

After that, this process is continued by mixing MOF with ethanol inside the autoclave and heated at 80°C in 3 hours to remove DMF or any other substance that were trapped in the pores of MOF. Finally, the MOF was cooled down, centrifuged, and dried again in the oven at 80°C for an hour. The result could be stored in a vial glass like in the Fig. 2.



Fig. 2: MOFs after strained

After doing the synthesis process, the adsorbent characterization was undertaken. We want to observe the chemical functionalities contained in our Bio-MOF based citric acid. Fourier Transform InfraRed (FTIR) measurements is carried out to determine the bonding ion that formed in the MOF using detectors, which are DTGS KBr, and KBr beam splitter.

Pore volume, pore radius and specific surface area of MOF were measured using a Quantachrome NOVA 2200e type instrument from N₂ isothermal adsorption at 77 K. The samples were degassed at 90°C¹⁷ for 3 hours before measuring adsorption. Before and after the degassing process, material weighing process was performed to find out the reduced mass. The isotherm data is used to calculate the surface area with the BET equation.

XRD measurements were carried out using a Shimadzu XRD-6000 diffractometer with a step size of 0.02 using monochromatic CuKα radiation (wavelength ¼ 0.154 nm) operated at 40 kV and 40 mA. Microstructure, morphology, and MOF particle size were determined by Scanning Electron Microscopy (SEM) using JEOL JSM-6510LA which was equipped with EDS (Energy Dispersive X-ray Spectroscopy) device to analyze chemicals composition in MOF. MOF thermal stability was tested using Thermal Gravimetric Analysis (TGA). MOF samples were heated to 900°C with the range of 10 °C / min under nitrogen flow. Then, MOF weight loss was measured as the function of temperature.

3. Results and Discussion

FTIR results showed the clusters formed on the MOFs material that has been synthesized where it compares the spectrum of pure citric acid (a) and the Bio-MOF Cr-CA

(b) representing on the Fig. 3. Visible reflection point of carbonyl group ($\text{C}=\text{O}$) 1767.90 cm^{-1} indicates the interaction of chromium molecules and carboxylic acid on the citric acid bio-ligand. Furthermore, the bond stretching with medium intensity at the wavelength of 3673.95 cm^{-1} indicates the presence of vibration of the hydroxyl group ($-\text{OH}$) citric acid on the Bio-MOF adsorbent representing the binding of bio-ligand in this Bio-MOF¹⁹). Other medium-intensity peaks are also observed at 2981 cm^{-1} and 2878 cm^{-1} reproduced from stretching vibrations of $\text{C}-\text{H}$ molecules. The high intensity peak at 2396 cm^{-1} is attributed to $\text{O}=\text{C}=\text{O}$ bond stretching. Other position wavenumbers have been described in Table 1.

Table 1: Adsorption band from FTIR test result compared to reference

Position wave number (cm^{-1})	Intensity Transmittance (%)	Reference adsorption band	note
3801.99	106.744	3700-3584	O – H (Alcohol – Free)
3673.95	104.273	3700-3584	
2981.01	101.906	3000-2840	C – H (Alkane)
2878.63	104.639	3000-2840	
2821.64	103.074	2830-2695	C – H (Aldehyde – Doublet)
2396.71	101.025	2349	O = C = O (Carbon Dioxide)
2161.03	95.554	2175-2140	S – C \equiv N (Thiocyanate)
2026.86	96.230	2140-1990	N = C = S (Isothiocyanate)
1976.35	96.820	2000-1650	C – H (Aromatic Compound – overtone)
1767.90	101.803	1800-1770	C = O (Conjugated Acid Halide)
1648.40	100.697	1650-1600	C = C (Conjugated Alkene)
1511.41	100.362	1550-1500	N – O (Nitro Compound)
1362.76	77.188	1390-1310	O – H (Sulfonate)
1131.59	98.248	1150-1085	C – O (Aliphatic Ether)
1055.23	90.107	1085-1050	C – O (Primary Alcohol)
823.07	91.605	$880 \pm 20 - 810 \pm 20$	C – H (1,2,4 – trisubstituted)

The thermal stability of the MOFs was measured by the

thermal gravimetric analysis. The whole graph could be seen on Fig. 4. The measurement was carried out in the temperature range of $50^\circ\text{C} - 900^\circ\text{C}$ with an increase of $10^\circ\text{C} / \text{minute}$. The first reduction in mass occurred during the process of increasing temperatures in the range of $130^\circ\text{C} - 430^\circ\text{C}$ by 0.125 mg . After that in the temperature range of 700°C the adsorbent started to decompose and leaved up to chromium oxide. Further, at the temperature of 800°C the remaining material were destroyed and at the temperature of 900°C , Bio-MOF Cr-CA had been burned (97.3% by weight mass was lost). In this test, we could probably assume the right temperature for degassing to keep the material from being decompose or burnt.

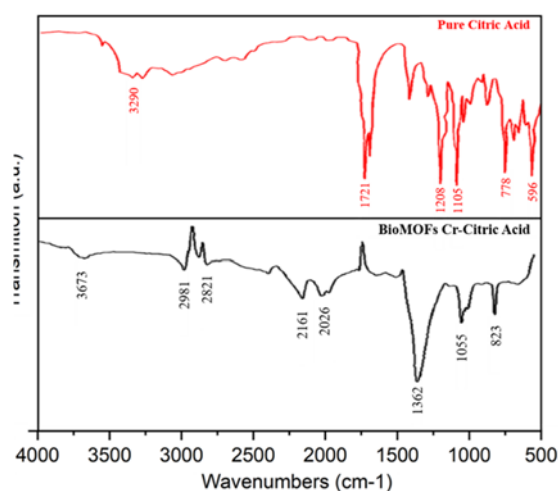


Fig. 3: FTIR result of Bio-MOF Cr-CA

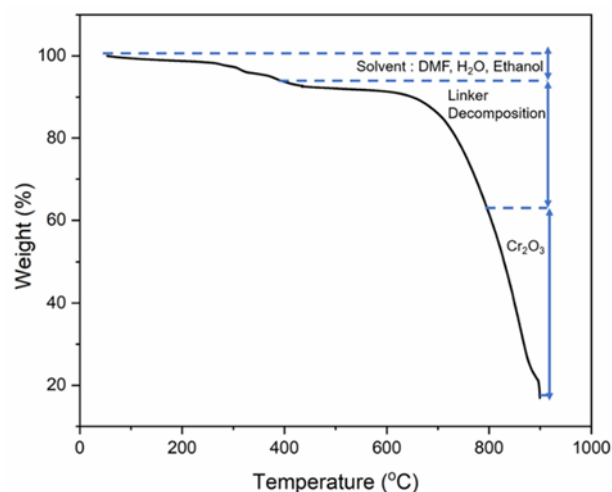


Fig. 4 : TGA result of Bio-MOF Cr-CA

In the SEM (Scanning Electron Microscopy) observation, the morphology of the MOFs material that has been formed can be seen. The results showed that the MOF material has the homogeneous shape. $1000\times$, $2500\times$, and $5000\times$ magnifications were observed in the range of $5\text{-}10\mu\text{m}$. SEM test results can be seen in Fig. 5, where MOF has a uniform shape and a large structure. The

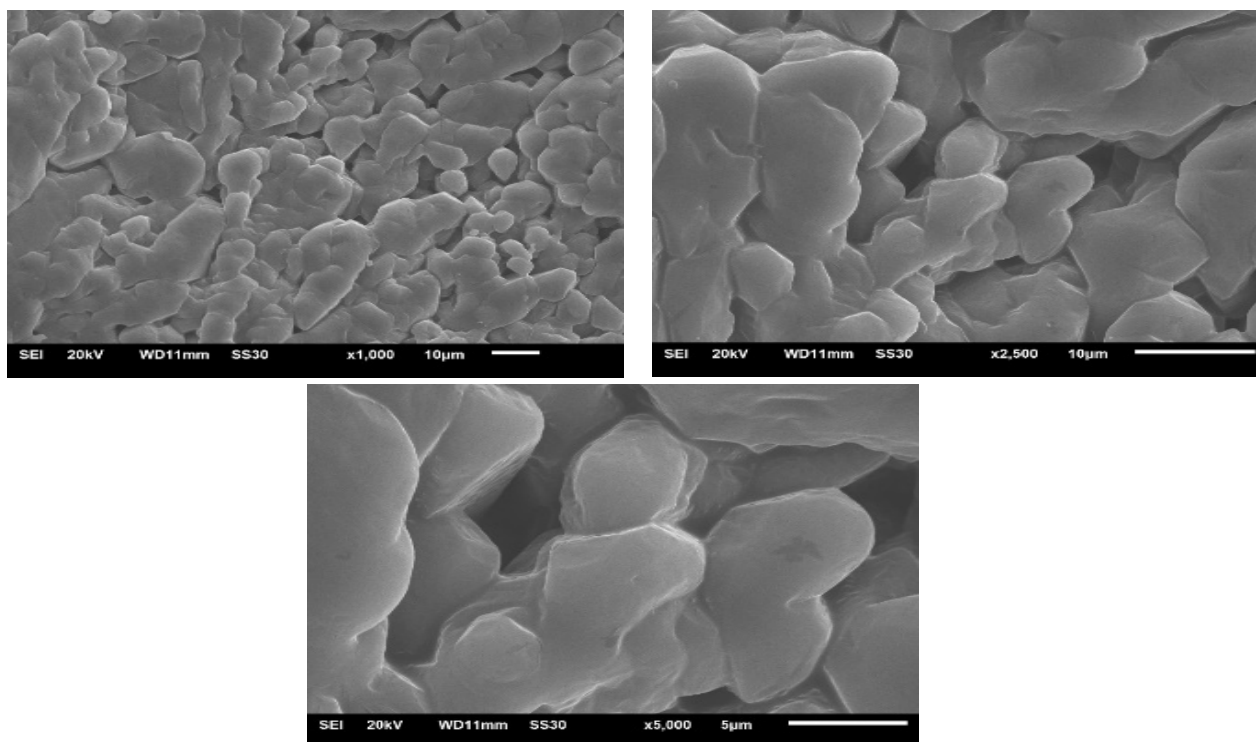


Fig. 5: SEM test result

particle structure of MOF could already be seen at 1000x magnification variation. The particle has uniformity size at 10μm. The morphology of the particles is observed having homogeneous grain with different sizes.

BET analysis was carried out at 11 points of N₂ adsorption at 77 K. Fig. 6 shows N₂ adsorption with the surface area of 35,550 m²/g. The surface area of Bio-MOF Cr-CA has the same range as other Bio-MOF groups such as Bio-MOF 14 and MPM-1-Cl with the pore volume of 0.05 cm³/g and it is still far from the surface area of non-renewable petrochemical MOFs¹⁷. The surface area is not the only things that affects gas adsorption capacity. From the results of our previous study, the surface area of the Bio-MOF did not have a significant effect on the CO₂ adsorption capacity⁸. On the contradictory to the pore

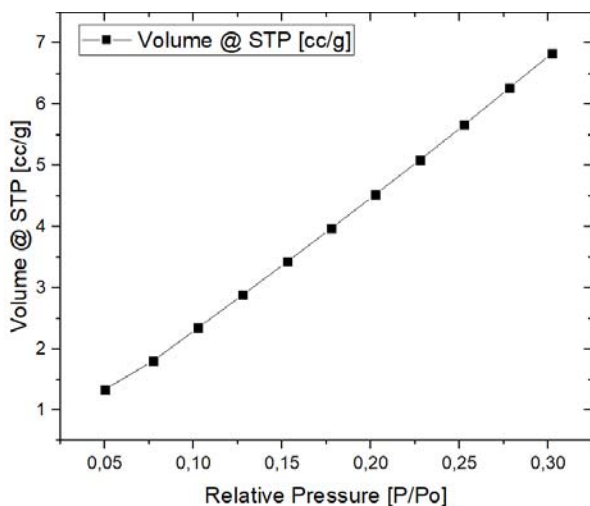


Fig.6: N₂ Adsorption for BET Measurement

volume, lowering the pore volume can enhance the interaction potential of the pore walls and CO₂ molecules^{20, 21}.

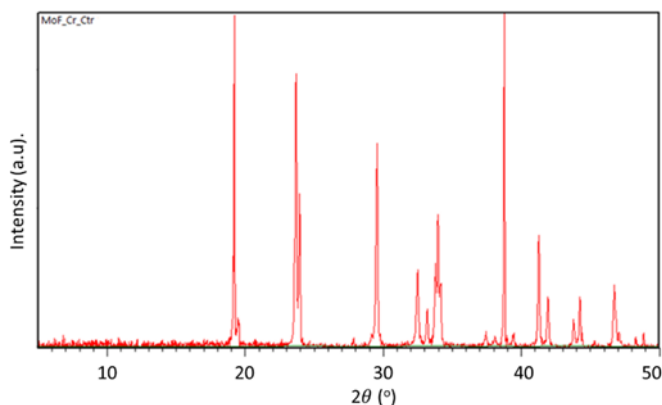


Fig.7: PXRD of Bio-MOF Cr-CA

The XRD investigation was performed to obtain the phase identification of crystalline material and showed the information on unit cell dimensions²². The peak list could determine the size and the micro stain of the sample²³. The XRD pattern of MOFs of Citric Acid is shown in Fig. 7. The high intensity peaks at the angle of 2θ represents good crystalline quality on Bio-MOF Cr-CA since the amorphous material will not produce sharp consistent peaks. Several sharp peaks were observed at the angles of 19°, 29°, and 34° having the same spectrum with other chromium nitrate as the metal constituent of the MOFs²⁴. The peaks at 24° and 39° represent the citric acid ligand in Bio-MOF with the same intensity in several reported

MOFs using citric acid bio-ligand^{25, 26}).

4. Conclusions

The Synthesis of Bio-MOF based Chromium nitrate and citric acid was successfully carried out at 120°C within 48 hours based on the results of the FTIR, SEM, TGA, and XRD. Based on the thermal gravimetric result, it was found that this Bio-MOF can maintain its structure up to 700°C. So, it can be concluded that the material has good resistance to high temperatures. Second step purification was performed to remove unreacted substances in the framework of the Bio-MOF. This synthesis should be optimized to meet the expectations of the porosity and the crystallinity.

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Nomenclature

MOF	Metal Organic Framework
CO ₂	Carbon Dioxide
CCS	Carbon Dioxide Capture System
FTIR	Fourier Transform Infra-Red
BET	Brunauer-Emmett Teller
SEM	Scanning Electron Microscope
TGA	Thermal Gravimetric Analysis

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